An Initial Look of Particulate Organic Matter Characteristics at Surface Sites During the 2006 MILAGRO Campaign

Xiao-Ying Yu,[1]* M. Lizabeth Alexander,[2] Timothy B. Onasch,[3] Nels S. Laulainen,[1] Robert Cary,[4] Douglas Worsnop,[3] Eben Cross,[5] Carl M. Berkowitz,[1]

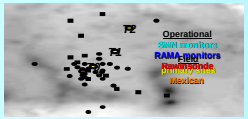
J. Christopher Doran,[1] Jerome Fast,[1] Rahul Zaveri,[1] Alexander Laskin,[2] Yuri Desyaterik,[2] Richard Coulter,[6] Timothy Martin,[6] and Jan Satola[7]

[1]*Atmospheric Science & Global Change Division, Pacific Northwest National Laboratory, Richland, WA 99352*
[2]*William R. Wiley Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352*
[3]*Aerodyne Research Inc., 45 Manning Rd., Billerica, MA 01821*
[4]*Sunset Laboratory, Inc.10160 SW Nimbus Ave., Suite F/8, Tigard, OR 97223-4338*
[5]*Department of Chemistry, Boston College, 2609 Beacon St., Chestnut Hill, MA 02467*
[6]*Atmospheric Physics Section, Argonne National Laboratory, ER/Building 203/J-155, 9700 South Cass Ave., Argonne, IL 60439*
[7] *Environmental Assessment & Exp, Battelle Columbus Operations (BCO), 505 King Ave., Columbus, OH 43201-2693*

E-mail: xiaoying.yu@pnl.gov

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Introduction



One of the main scientific objectives was to study the evolution of aerosol properties as they age. Aerosol optical, physical, and chemical properties were measured at two ground sites, T1 and T2, downwind of Mexico City (T0).

Field Site and Experimental Set-up

1. T1 and T2 Field Sites

Overview of the MILAGRO T1 Site

The PNNL Research Trailer at T2

The PNNL Research Trailer at T1

The T1 site was located at the Tecamac University (latitude 19.703 N, longitude 98.982 W, altitude of 2273 m) north of the main metropolitan area of Mexico City. Urban plume from the Mexico City (T0) was expected to transport and influence this site frequently. The T2 site was 35 km to the northeast of T1 at Rancho la Bisnaga in Pachuca (latitude 20.010 N, longitude 98.909 W, and altitude 2542 m). Semi-continuous and continuous sampling started on March 9, 2006 and ended on March 30, 2006 at T1, and started on March 9, 2006 and ended on March 29, 2006 at T2.

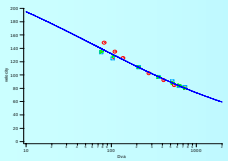
2. Instrument setup

We utilized a suite of instrumentation at T1 and T2 sites. More detailed information on the ASP supported instrumentation is available elsewhere.[2] Briefly, two identical aerosol sampling racks containing a nephelometer (TSI Model 3563), a light absorption photometer Particle Soot Absorption Photometer, (PSAP, Radiance Research) and a condensation nucleus counter (TSI Model 3010) were deployed at T1 and T2. In addition, two OC/EC (Sunset Laboratory) units were deployed simultaneously at T1 and T2. An Aerodyne c-ToF Aerosol Mass Spectrometer (c-ToF AMS) was also deployed at T1.

The c-ToF AMS Schematic Diagram[3]

The c-ToF AMS Field Setup

The Sunset OC/EC Field Setup



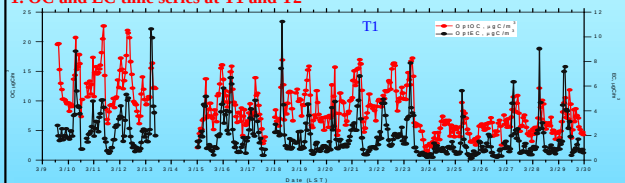
The PToF calibration at T1 was shown here. The vg,a = 308.33 ± 8.38, vg,i= 30 ± 0, b = 0.5 ± 0, D* = 35.518 ± 3.09. Details of the fitting parameter definitions were described elsewhere.[3]

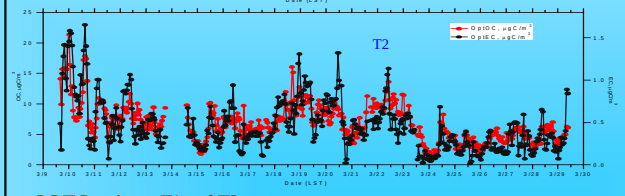
The Sunset OCEC analyzers use thermal-optical methods to determine organic and elemental carbon compounds. Semi-continuous measurements of $PM_{2.5}$ OCEC were obtained hourly, with 45 minutes sampling and 15 minutes analysis and cooling. Each OCEC unit was calibrated using external standard filters on-site before ambient sampling. The external standard was analyzed in off-line mode. The data acquisition parameters were adjusted after the calibration to reflect the known OC/EC ratio. The estimated detection limit was 0.02 μgCm^{-3} and the estimated standard deviation of the OCEC measurement was 0.02 μgCm^{-3}. Quartz filters were changed every few days before a significant reduction in the intensity of the laser signal used for the optical corrections was observed. A blank was scheduled at midnight (LST) daily.

The c-ToF AMS was recently developed combining the successful technical know-how of the Aerodyne Q-AMS including aerosol sampling, sizing and evaporation/ionization, an orthogonal extraction time-of-flight mass spectrometer (TOFWERK) and fast data acquisition hardware. It can provide information on non-refractory aerosol mass concentrations approximately PM_1, chemically speciated size distribution, and single particle. The PNNL c-ToF AMS was deployed with 5 minute time average switching between the mass spectrum (MS) and the particle time-of-flight (PToF) mode. The PToF calibration conducted at T1 was shown here.

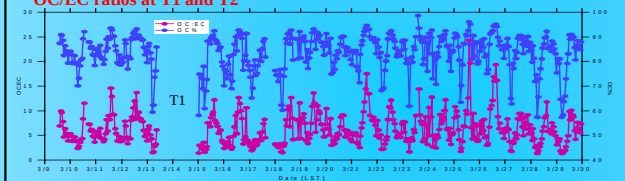
Preliminary results

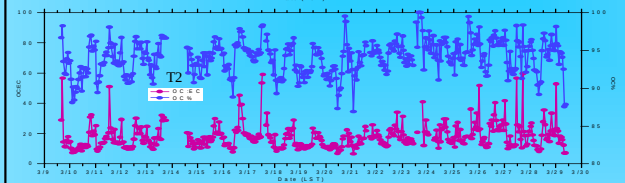
1. OC and EC time series at T1 and T2

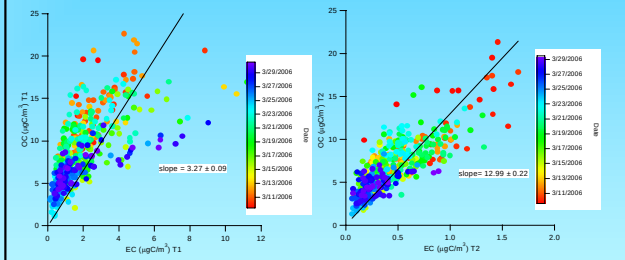




OC/EC ratios at T1 and T2



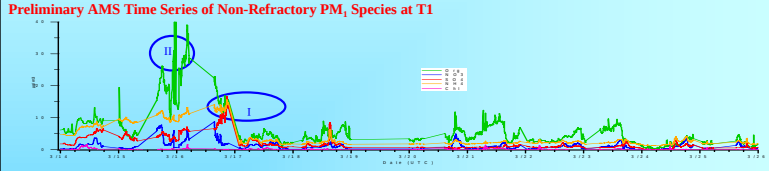




Time series of OC and EC at T1 and T2 were plotted. The average OC and EC mass loadings were 8.95 $\mu gC/m^3$ and 1.94 $\mu gC/m^3$ respectively at T1; and 7.01 $\mu gC/m^3$ and 0.45 $\mu gC/m^3$ respectively at T2. When looking at the OC/EC time series, some of the spikes were resulted from extremely low EC values. Therefore a better way to look at the OC/EC ratio is using the linear least-squares regression analysis. The fitting slope for OC:EC is 3.27 at T1 and 12.99 at T2. However, fitting the data per day could result in different slope values. The average OC% (OC%=OC/TC*100%) was 83% and 94% at T1 and T2 respectively. All of the above facts strongly indicate the formation of secondary OC at T1 and T2. It is known that OC/EC ratios vary considerably from source to source, i.e., they are influenced by meteorology, diurnal and seasonal fluctuations in emissions, and influence of local sources. This data set presents a good opportunity for in-depth investigation of these factors and their impact on the secondary organic aerosol formation.

2. The AMS Measurement

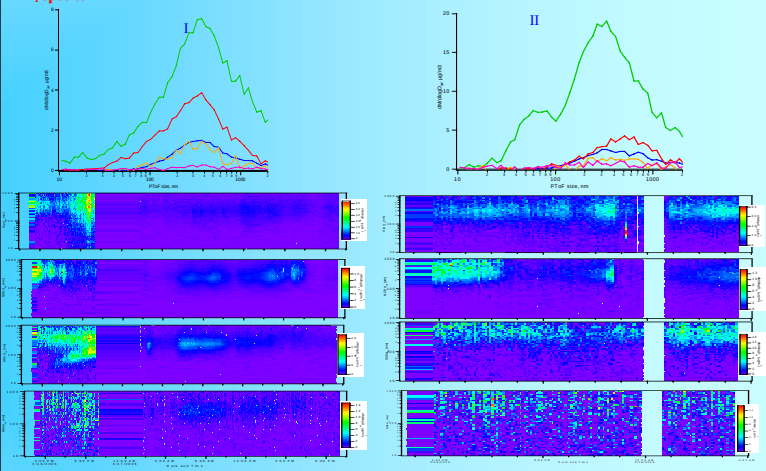
Preliminary AMS Time Series of Non-Refractory PM_1 Species at T1



Preliminary time series from March 14 to March 26 was depicted. Organic was the major component of the total mass loading at T1. We selected two segments of data to look into the particle size distribution.

Preliminary sample AMS size distribution of Non-Refractory

PM_1 species



The preliminary size distribution of the main NR-PM_1 species as a function of time and size at T1 during case I and II was shown above. Case I occurred from March 16 to March 17, 2006 (UTC), and II from March 15 to March 16, 2006 (UTC). The average size distribution observed in case I is similar to previous findings in the MCMA-2003.[4] We observed bimodal size distribution in case II, which indicates new particles formation.

Conclusions and Future Work

Clearly more work is needed to finish analyzing the observation obtained at T1 and T2 during the 2006 MILAGRO field campaign. Specifically, we will look into the OC and EC emission sources, transport, and transformation between T1 and T2. Another major task is to fully understand the wealth of information the c-ToF AMS provided at the T1 site. One of our main objectives is to combine the observations and implement modeling approach to better understand aerosol formation, transformation, and transport.

References

1. C. Doran et al., J.C. Doran, J.C Barnard, J.D. Fast, E.I. Kassianov, N.S. Laulainen, M.S. Pekour, W.J. Shaw, X-Y Yu, W.P. Arnott, L.Paredes-Miranda, R. Coulter, T. Martin, L. Kleinman, S. R. Springston, and R. Cary, The T1-T2 aerosol study, submitted, Atmospheric Chemistry and Physics
2. M.S. Pekour, J.C. Barnard, L. K. Berg, J.C. Doran, N.S. Laulainen, W.J. Shaw, and X.-Y. Yu, ASP Infrastructure Project Support of the MAX-MEX Field Campaign, poster presentation at the 2006 ASP workshop
3. F. Drewnick, S.S. Hings, P.F. DeCarlo, J.T. Jayne, M. Gonin, K. Fuhrer, S. Weimer, J.L. Jimenez, K.L. Demerjian, S. Borrmann, D.R. Worsnop. A new Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS) – Instrument Description and First Field Deployment. *Aerosol Science and Technology*, 39:637–658, 2005
4. Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., et al., Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmos. Chem. Phys., 6:925-946, 2006

Acknowledgements

Support of this research was from the DOE ASP program for the PNNL research team.